## This Page Is Inserted by IFW Operations and is not a part of the Official Record

### **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

### IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

### (12) UK Patent Application (19) GB (11) 2 260 985(13)A

(43) Date of A publication 05.05.1993

(21) Application No 9222907.9

(22) Date of filing 30.10.1992

(30) Priority data (31) 07785592

(32) 30.10.1991

(33) US

(71) Applicant

**Bristol-Myers Squibb Company** 

(incorporated in the USA - Delaware)

345 Park Avenue, New York, New York 10154, **United States of America** 

(72) Inventors Janusz Jachowicz Chittamuru Ramireddy

(74) Agent and/or Address for Service Mathys & Squire 10 Fleet Street, London, EC4Y 1AY, **United Kingdom** 

(51) INT CL5 C08F 220/60, A61K 7/06, C08F 220/34 226/02

(52) UK CL (Edition L)
C3P PDH PDK PDT U1S S1302 S1343

(56) Documents cited

GB 2136689 A

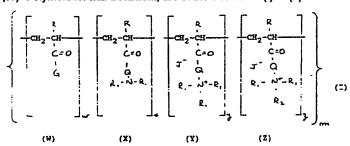
EP 0200903 A2 EP 0464957 A2

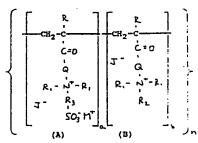
US 4818245 A

(58) Field of search UK CL (Edition K) C3P PDH PDT PDW INT CL<sup>5</sup> COSF

### (54) Internally charged hydrophobically modified copolymers

(57) Polymers for hair treatment, are of the structures (I) or (II):-





wherein each G is selected from -OH and OR<sub>3</sub>SO<sub>3</sub>-M\*;

each Q is selected from -OR<sub>3</sub>-; -NHŘ<sub>3</sub>-; -OR<sub>3</sub>NHCONHR<sub>3</sub>-; and -OR<sub>3</sub>NHCOOR<sub>3</sub>-;

each R is H or methyl;

each R, is an alkyl of from 1 to 4 carbons, especially methyl;

each R<sub>2</sub> is an alkyl of from 10 to 24 carbons, preferably from 12 to 18 carbons

each R, is an alkyl n radical of from 2 to 4 carbons, especially ethyl;

J is an anion especially chloride, bromide or iodide;

M is a cation, especially sodium or potassium;

w, x, y, and z, a and b designate the number of moles of the monomeric units in accordance with the mole fraction and mole ratio constraints: w/x and w/y are about 0.4 or greater; w/z is from about 199:1 to about 0.67:1; w/(x+y+z) is from about 199:1 to about 0.25:1, and a/b is from about 199:1 to about 2.3:1, w, z, a and b being positive, and x and y being less than or equal to about 0.5, and

m and n are numbers designating the degree of polymerization.

985

(II;

## INTERNALLY CHARGED HYDROPHOBICALLY MODIFIED COPOLYMERS

### Field of Invention

The present invention concerns hydrophobically modified copolymers for conditioning hair, the copolymers being characterized by the presence of internally charged ionic species. More specifically, the invention concerns such copolymers and compositions containing same for use in cosmetics, in particular, for use in the treatment of hair.

### Background of Invention

Polymers useful in preparing hair-treating compositions are known in the art. These known polymers include homopolymers and copolymers, and may be anionic, cationic, amphoteric or zwitterionic in character.

U.S. 4,402,977 to Grollier et al discloses amphoteric polymers for use in the treatment of keratin fibers, especially in combination with anionic polymers. U.S. 4,818,245 to Jachowicz et al discloses certain cationic polymers having a hydrophobic moiety, the polymers being suitable to reduce static electricity in the hair. U.S. 4,590,249 to Cabestany et al discloses cationic ampholytic tetrapolymers useful in treating hair. U.S. 4,767,616 to Kubota discloses hair conditioning resins prepared by modifying a copolymer with a zwitterionic agent. GB 2,136,689 discloses compositions for conditioning hair which contain at least one anionic polymer and at least one cationic or amphoteric polymer. GB 1,368,495 discloses hair setting compositions incorporating copolymers including a zwitterionic monomer. U.S. 4,650,848 to Schultz et al discloses certain terpolymers useful as viscosifiers. U.S. 4,710,555 to Pfeiffer et al discloses certain tetrapolymers useful as viscosity enhancers. U.S. 4,730,028 to Bock et al discloses cationic terpolymers of a zwitterionic character.

### Summary of Invention

The hydrophobically modified copolymers of the present invention incorporate monomeric groups providing species that are internally charged. In one embodiment of the invention, the polymers are copolymers, terpolymers or tetrapolymers which comprise (a) a strongly cationic hydrophobic monomer, (b) either

a weakly or a strongly anionic monomer, (c) optionally, a strongly cationic hydrophilic monomer, and (d) optionally, a weakly cationic monomer.

In another embodiment the copolymers of the present invention comprise (e) a strongly cationic hydrophobic monomer and (f) a zwitterionic monomer.

The copolymers of the present invention, in view of the plural nature of their ionic makeup, provide great flexibility in preparing cosmetic formulations. Thus, for example, the copolymers are sensitive to pH of the cosmetic composition, which may be varied, along with the molar ratios of the monomers, to obtain desired copolymer attributes.

The preferred use for the copolymers of the present invention lies in the treatment of hair. In particular, in view of the hydrophobic monomer incorporated within each class of copolymer set forth above, the copolymers of the present invention are particularly useful in the conditioning of hair, their application to hair by means of a cosmetically acceptable vehicle enhancing the hair's softness, antistatic and tactile properties.

### <u>Detailed Description of Invention</u>

The two classes of hydrophobically modified copolym rs

previously referred to may be represented structurally as follows.

$$\begin{cases}
\begin{bmatrix}
R \\
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\end{bmatrix}
\begin{bmatrix}
R \\
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH \\
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}
CH_2 - CH
\end{bmatrix}
\begin{bmatrix}$$

wherein each G is selected from -OH and -OR<sub>3</sub>SO<sub>3</sub>-M<sup>+</sup>; each O is selected from -OR<sub>3</sub>-; -NHR<sub>3</sub>-; -OR<sub>3</sub>NHCONHR<sub>3</sub>-, and -OR<sub>3</sub>NHCOOR<sub>3</sub>-;

each R is H or methyl;

each R<sub>1</sub> is an alkyl of from 1 to 4 carbons, especially methyl;

each R<sub>2</sub> is an alkyl of from 10 to 24 carbons, preferably from 12 to 18 carbons

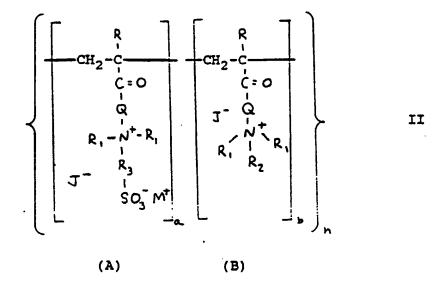
 $\operatorname{each} R_3$  is an alkylene radical of from 2 to 4 carbons, especially ethyl;

J is an anion, especially chloride, bromide or iodide;

M is a cation, especially sodium or potassium;

w, x, y and z are integers designating the number of moles of the monomeric units, and m is a number designating the degree of polymerization.

and



wherein R,  $R_1$ ,  $R_2$ ,  $R_3$ , Q, J, and M have the definitions set forth above; a and b are integers designating the number of moles of the monomeric units, and n is a number designating the degree of polymerization. (W), (X), (Y), (Z), (A) and (B) designate specific monomeric groups with the copolymers.

In Polymer I the monomers (W) and (Z) are deemed essential and the monomer (Y) is preferably incorporated, while the monomer (X) is optional. Monomer (Z), in view of the long chain alkyl group  $R_2$ , is hydrophobic, and is also strongly cationic in view of the positively charged nitrogen. Monomer (Y) is also strongly cationic, but is hydrophilic by virtue of the short chain alkyl groups substituted on the quaternary nitrogen.

Monomer (X) is weakly cationic, the nitrogen not being quaternized, and is also hydrophilic.

Monomer (W) may be weakly or strongly anionic, depending upon the choice of the substitutent group G. Thus, when G is -OH, the monomer unit (W) contains a weakly ionizable carboxylic acid radical. When G is -OR<sub>3</sub>SO<sub>3</sub>-M<sup>+</sup>, the monomer unit (W) is readily ionized, and (W) is strongly anionic. Both weakly and strongly anionic monomer units (W) may be present in the copolymer.

The electrostatic character of the Polymer I is determined by the molar ratio of anionic to cationic groups, i.e., the ratio w/(x + y + z), and by the type of substituent group present in the anionic monomer (W). The more highly cationic copolymers are preferred for use as hair conditioning agents, while the more highly anionic copolymers may be employed, as further disclosed below, in temporary hair color rinses.

The ratio w/(x + y + z) is generally within the range of from about 199:1 to about 0.25:1.

In Polymer II the monomers (A) and (B) are both essential. Monomer (B), in view of the long chain alkyl group  $R_2$  and the positively charged nitrogen, is both cationic and hydrophobic. The monomer (A) is zwitterionic. That is, monomer (A) is an internal salt by virtue of  $-so_3^-M^+$  group.

The Polymers I and II, because both positively and negatively charged moieties are present, may each be regarded as amphoteric, i.e., sensitive to the pH of the media in which they are placed, as hereinafter described.

The Polymers I and II may be water-soluble, waterdispersible or water-insoluble, depending upon the mole fraction of the monomers (Z) or (B). Thus, for a water-soluble copolymer, the mole fraction of monomers (Z) and (B) should be less than about 0.1, preferably within the range of from about 0.02 to about 0.08. Above a mole fraction of about 0.1 solubilization becomes difficult, such copolymers being either water-dispersible or water-insoluble. The water-soluble copolymers are suitable for use in aqueous cosmetic compositions without resort to the use of a surfactant or organic solvent solubilizer. The water-dispersible and water-insoluble copolymers may be employed in nonaqueous cosmetic compositions, or in aqueous compositions also containing an emulsifying surfactant or a hydrotrope, or which incorporate a nonaqueous organic solvent such as a C1 to C6 mono- or polyhydric alcohol, preferably ethanol, isopropanol, ethylene glycol or propylene glycol.

The ionic nature of the Polymers I and II depends upon the relative proportions of the anionic, cationic or zwitterionic

monomeric units, the strength of the ionic charge associated with a particular monomeric unit, and the pH of the media containing the copolymer. Thus, a Polymer I having a high molar ratio of strongly cationic monomer units, such as units (Y) and (Z), to weakly anionic monomer units, such as (W) when G is -OH, is generally cationic except at high pH values. Conversely, a Polymer I having a low molar ratio of strongly cationic monomer units to strongly anionic monomer units, such as (W) when G includes SO<sub>3</sub>, is generally anionic. For Polymer II, the copolymer is typically cationic.

This sensitivity to pH permits the formation of copolymers that are amphoteric or cationic in acid media and anionic in basic media, when the ionic strengths and molar ratio of the cationic and anionic monomer units are in balance.

The suitable mole fractions of each of the monomer units are set forth below.

### TABLE I

Monomer	Monomer Unit Mol Broad	Preferred
(W)	0.2-0.995	0.4-0.95
(X) or (Y)	0-0.5	0.1-0.4
(Z)	0.005-0.3	0.05-0.2
(A)	0.7-0.995	0.8-0.95
(B)	0.005-0.3	0.05-0.2

The cationic/anionic mole ratios for the monomer units of Polymer I are set forth below:

TABLE II

	Mole R	atio
	Broad	Preferred
w/x	≥0.4:1	9.5:1-1:1
w/y	≥0.4:1	9.5:1-1:1
w/z	199:1-0.67:1	19:1-2:1
w/(x - y + z)	199:1-0.25:1	19:1-0.67:1
a/b	199:1-2.3:1	19:1-4:1

The degree of polymerization m is such that the Polymers I of the present invention have a molecular weight from about 2000 to about  $2 \times 10^6$ , preferably from about  $10^4$  to about  $10^6$ . For Polymer II, the degree of polymerization n is such that these polymers have a molecular weight of from about 2000 to about  $2 \times 10^6$ , preferably from about  $10^4$  to about  $10^6$ .

The character of group Q does not significantly affect the properties of the copolymer. In some cases it may provide polymer hydrolytic stability or compatibility with anionic surfactants. Thus, polymers with amide groups in the side chain, e.g., Q is -NHR<sub>3</sub>-, are usually characterized by a better hydrolytic stability than those with ester groups, e.g., Q is -OR<sub>3</sub>-. Cationic polymers with a urethane group, e.g., Q is -OR<sub>3</sub>NHCOOR<sub>3</sub>-, or a urea group, e.g., Q is

'R3NHCONHR3-, are characterized by increased compatibility with anionic surfactants.

### Preparation of the Monomers

Generally, the Polymers I and II are prepared by free radical polymerization of corresponding monomers.

Methacrylic acid, potassium 3-sulfopropylmethacrylate, dimethylaminoethylmethacrylate, dimethylaminopropylmethacrylamide, trimethylpropylmethacrylamide ammonium chloride are commercial products available from Aldrich Chemical Co. or Alcolac, Inc.

Urethane and urea-containing monomers and their polymers may be prepared from isocyanoethylmethacrylate using syntheses disclosed in commonly owned United States Patent 5,149,752.

Cationic surfactant monomers alkyl-dimethyl-C<sub>1-4</sub>-methacrylate ammonium halides, may be prepared by the quaternization of the corresponding amines in acetonitrile. The products may be purified by recrystallization from acetonitrile.

Sulfobetaine-containing monomers may be prepared by reacting

the corresp nding amines with propane sultone. The synthetic procedure is illustrated with the following example:

Dimethylaminopropyl methacrylamide (85.1 g, 0.5 mole), m-dinitrobenzene (50.5 mg, 3 x 10<sup>-4</sup> moles) and 100 ml acetonitrile were placed in a round-bottom flask placed in an ice-water bath. Propane sultone (67.18 g, 0.55 mole) dissolved in 25 ml acetonitrile was added dropwise and resulted in the formation of white precipitate. After the addition was completed, the stirring was continued for a few hours at 60 C°, followed by addition of 100 ml of AcOEt. The product was filtered off and washed with acetone.

### Synthesis of Polymers

All copolymerizations (Polymers I and II) were performed in an aqueous medium by using potassium persulfate as an initiator. Typical experimental procedures are illustrated with the synthesis of Polymer I-3.

Polymer I-3 (see Table V-A) is prepared as follows: potassium 3-sulfopropylmethacrylate (49.2 g, 0.2 mole), dimethylamino-ethylmethacrylate (31.4 g, 0.2 mole) and hexadecyldimethylethylmethacrylate ammonium bromide (17.5 g, 0.038 mole) were dissolved in 150 g of deionized water. Potassium persulfate (500 mg) was added and the copolymerization was performed at 60°C for four hours. The product is a copolymer gel which can be diluted with water.

Polymers suitable in the practice of the present invention are illustrated in Tables V-A and V-B below (R being  $-CH_3$  in each instance).

TAULE V=A

			1 158X [6]			
M nomer Unit: Submetituent: Group.	<b>, 198</b>	<b>ca</b> -	et~	<b>₩</b>	ភា	<b>G</b> I
(M): G	HO	110	0(CII <sub>2</sub> ) <sub>2</sub> 50 <sub>3</sub> K	110	0(CII <sub>2</sub> ) <sub>2</sub> SO <sub>3</sub> K	0(CII <sub>2</sub> ) <sub>2</sub> SO <sub>1</sub> K
0 : (x) . B	O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub>	0(CII <sub>2</sub> ) <sub>2</sub> CII <sub>3</sub> , CH <sub>3</sub>	O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub>		٥(دااء) ۽	
(Y): Q R <sub>1</sub>				o(сн <sub>2</sub> ) <sub>2</sub> сн <sub>3</sub> , сн <sub>3</sub> , сн <sub>1</sub> си <sub>3</sub> so <sub>4</sub>	0(CII <sub>2</sub> ) <sub>2</sub> CR <sub>3</sub> , CH <sub>3</sub> , CII <sub>3</sub> CII <sub>3</sub> SO <sub>4</sub>	
(2): Q R <sub>1</sub> R <sub>2</sub>	O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> C <sub>16</sub> H <sub>31</sub> Br	o(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br <sup>-</sup>	O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br <sup>-</sup>	0(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> C <sub>16</sub> H <sub>31</sub> Br	0(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br <sup>-</sup>
Polymer <b>Chara</b> cterization	ua					
W/x W/y W/E W/(x+y+2) ccharacter	1. 10. 0.91 cationic at pH<10	1. 20. 0.95 cationic at pH<10	1. 5.26 0.84 anionic at pH*4	10 0.91 cationic at pikio	4.26 5.41 0.71 cationic at all pil	5.11 5.11 anionic at all pil

# TABLE V-B

Polymers II

	O(CH <sub>2</sub> ) <sub>2</sub> NIICONII(CH <sub>2</sub> ) <sub>2</sub> <sup>3</sup> CH <sub>3</sub>	$O\left(\text{CH}_2\right)_2$ NHCONH $\left(\text{CH}_2\right)_2$ CH $_3$ C $_{16}^{\text{H}}_{33}$ Br $^-$	10 Cationic at all pH
<b>(7)</b>	o (сн <sub>2</sub> ) <sub>2</sub> Niicoo (сіі <sub>2</sub> ) <sub>2</sub> сн <sub>3</sub> , сн <sub>3</sub> (сн <sub>2</sub> ) <sub>2</sub>	O(CH <sub>2</sub> ) <sub>2</sub> NHCOO(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br <sup>-</sup>	10 Cationic at all pil
<del>~1</del>	NH (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> , CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	NH(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> , CH <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br <sup>-</sup>	10 Cationic at all pH
Monomer Unit: Substituent <u>Group</u>	(A) : Q R <sub>1</sub> R <sub>2</sub>	(B): Q R <sub>1</sub> R <sub>2</sub> J	Polymer Characterization a/b character

The following examples are illustrative of the present invention.

### Example 1

This example is illustrative of the suitability of polymer of the invention as hair conditioners.

The following compositions were prepared incorporating the Polymer identified in Table V-A.

Compositions	Conce	entrat	ion, :	vt. %
	1*	2	3	4
Stearalkonium chloride	1.0	•	-	-
Polymer I-1	-	1.0	-	-
Polymer I-3	-	-	1.0	-
Polymer I-4	-	-	-	1.0
Water	<<	Q.S.	100%	>>

<sup>\*</sup>Control incorporating stearalkonium chloride as a conventional conditioner.

These compositions were applied to dyed hair tresses and maintained in contact with the hair for 3 minutes, after which the compositions were rinsed off. The degree of conditioning as evaluated blindly in two judgments who assessed qualitatively the work to wet comb the hair tresses. The judg s compared these unconditioned tresses to an oxidatively dyed hair tress

which was defined as having a score of zero. The treated hair tresses were given a rating of between a value of zero and 5, the 5 rating being "very easily combed." The ratings were made after the conditioning treatment and again after the treated tresses were twice shampooed. The results are as follows.

Composition	<u>Condition</u> :	ing Score (Average)
	<u>Initial</u>	After 2 Shampoos
<u>1</u>	5	0
2	3.75	3.75
3	0.5	0.5
4	3.25	0.5
Dyed Hair	0	0

Polymer I-1 has predominantly cationic character at pH below 10, contains weaky acidic carboxyl groups, and has rather low solubility in the aqueous medium (forms gels). In consequence of this, it can bind to hair in relatively large quantities, and is not easily removed by shampooing. In view of its good conditioning properties and high durability, Polymer I-1 could be appropriate for hair damaged after chemical treatments. Polymer I-4 (Composition 4) is also suitable but does not provide durability because of increased, as compared to Polymer I-1, solubility in water. This polymer could be useful in formulating day-to-day use conditioner for normal or slightly damaged hair because of its good, after-treatment conditioning properties, and no build-up characteristics. Polymer I-3 (Composition 3) provides a lesser conditioning benefit because it is characterized by the overall anionic charge above pH 4 and

relatively high solubility in aqueous media. This kind of a material is appropriate for use in mild conditioners such as, for example, for thin and undamaged hair.

### Example 2

The following are examples of conditioning shampoo composition containing a polymer of class I of the present invention, which compositions are especially useful for bleached or dyed hair, e.g., following such treatments whether at home or in a salon.

<u>Composition</u>	1	2	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Sodium lauryl sulfate	16.16	15.45	15.26	15.04	-	-
Sodium lauryl ether sulfate	-	-	-	-	13.79	14.52
Lauramide DEA	-	5.02	4.96	5.0	5.02	-
Polymer I-1	1.57	_	-	-	-	-
Polymer I-2	-	0.75	_	-	-	_
Polymer I-3	-	-	1.49	-	-	-
Polymer I-4	-	_		1.50	1.50	0.79
DMDM hydantoin	0.31	0.30	0.30	0.30	0.30	0.32
Methyl paraben	0.10	0.10	0.10	0.10	0.10	0.11
Citric acid	0.63	-	1.19	0.30	-	-
Water (deionized)			<<< Q	.s. 100	<b>የ &gt;&gt;&gt;</b>	
pH	4.5	5.5	4.5	4.5	5.5	5.0

Formulations containing predominantly cationic Polymers I-1, I-2 and I-4 provide greater conditioning that those including anionic Polymer I-3. Advantageously, no build-up of polymers on hair surface was observed after multiple shampooing with Compositions 1-6. Surprisingly, the cationic polymers I-1, I-2 and I-4 were not deactivated by the anionic surfactants in the shampoo composition.

### Example 3

The following are examples of conditioning shampoos containing polymers in class I, which compositions are especially used on virgin hair, e.g., as home shampoos.

Composition	<u>1</u>	<u>2</u>
Cocoamphocarboxypropionate	14.86	14.81
Lauramidopropylamine oxide	4.76	
Lauramide DEA	4.76	4.75
Polymer I-2	4.43	-
Polymer I-4	-	1.42
DMDM Hydantoin	0.10	0.09
Methyl paraben	0.19	0.19
Water (deionized)	<< Q.S.	100% >>
Нд	8	8

Both compositions, used as shampoos, improve the combability of untreated hair. Composition 2 provides particularly good conditioning. Its effect is dependent upon the duration of rinsing with water after the shampooing, with prolonged rinsing reducing the conditioning benefit of the treatment.

### Example 4

This example illustrates the utility of the polymers of the present invention in the temporary coloring of hair.

6.2 g of a homogeneous Premix A comprising 16.13% propylene glycol; 3.22% methyl paraben and the remainder water was prepared, and blended with 10 g of a 10% solution of Polymer I-3 and also with 70.33 g of Premix B comprising 0.426% Natrosol 250, 0.0426% 2-aminoethylpropanol and the remainder water. 86.53 g of this homogeneous mixture was blended with 12.98 g of a dye mix comprising 0.516% disodium EDTA, 5.287% temporary dyes, 0.4 g DMDM hydantoin, 0.1 g citric acid and the remainder water.

The resulting composition is a viscous, homogeneous solution without precipitate. Blended gray hair tress was immersed in the formulation, the excess of the treatment was squeezed off, and the hair was dried. Color saturation was good. A "bleed-off" test was performed by immersing the hair tress in water for 15 seconds, and then visually evaluating the degree of coloration of the aqueous solution. The composition containing polymer I-3 showed smaller "bleed-off" effect than compositions comprising in lieu of this polymer such conventional water-soluble polymers as poly(vinyl pyrrolidone), poly(methylvinylether-monoethyl maleate) (Gantrez), poly(adipic acid-dimethylaminohydroxypropyldiethylenetriamine) (Cartareten), hydroxyethylcellulose or an amphoteric polymer containing only (W) and (X) monomers, G being  $-0(CH_2)_2SO_3K$ , Q being  $-OCH_2CH_2-$ ,  $R_1$  each being  $CH_3$  and w/x = 1. Compositions containing I-5 and I-6 in lieu of Polymer I-3 were prepared, and performed similarly. The results clearly demonstrate superiority of the hydrophobically modified polymers of the present invention over the conventional water-soluble polymers, in a hair dyeing process.

### Example 5

The Polymer I-6 (Table V-A) was used in a 1% aqueous solution as a hand lotion, and was found to impart good tactile properties to the treated skin.

### Example 6

The following example illustrates the use of Polymers I-3 and I-5 as a hair setting agent in an aerosol composition. Advantageously, the compositions do not require the incorporation of a foaming agent such as a low-molecular-weight surfactant inasmuch as the polymers themselves provide this functionality.

Ingredient		ration,
Part A - Concentrate	<u>.</u>	<u> 2</u>
Polymer I-3 Polymer I-5 Deionized Water	2 - 98	- 2 98
Part B - Aerosol Product		
Concentrate Propellant*	92 8	9 <b>2</b> 8

\*3:1 ratio of Fluorocarbon 152A and isobutane.

Discharge of the aerosol product produced a stable, nonsticky, creamy foam. The product was easily applied to hair and the hair was easy to comb.

The mousse products of the present invention are evaluated for curl-holding ability by their application to hair under controlled conditions. Curl relaxation is then measured on exposure to high humidity and compared with appropriate standards. For example, 0.3 g of mousse product is applied and

spread through ut a 2 g swatch of hair. The hair tress is curled n a mandrel and dried at ambient conditions. Curl relaxation that consists of periodic measurement of the curl fall is then performed under exposure to high humidity (90-95% R.H.). The results presented in the table shown below (percent and retained as a function of time) represent an average per six hair swatches.

Time	Perce	nt Curl Retain	ed
(hours)	Control*	Comp. 2	Comp. 2
-0-	100	100	100
0.02	61.36 ·	75.18	70.92
0.5	22.72	39.75	33.52
1	19.05	34.91	29.11
2	18.32	31.20	24.67
3	16.05	26.89	22.15
4	13.93	25.68	21.51
6 .	13.93	23.85	<b>-</b>
24	10.99	19.52	19.61 15.81

### \*Water set

Percent curl retained is calculated as follows:

% Curl Retention = 
$$\frac{(L - L_1)}{(L - L_0)}$$
 x 100

### wherein:

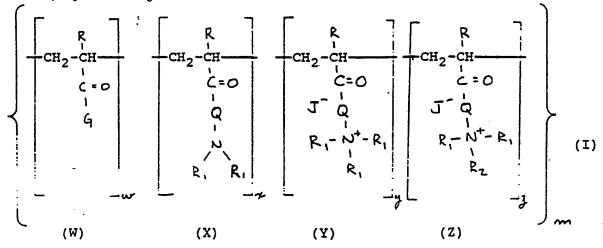
L = the length of hair fully extended (standard 6" length).

 $L_{\rm O}$  = the length of the hair curl immediately upon removal from the mandrel.

 $L_{\text{t}}$  = the length of the hair curl after exposure at time t. This method may also be used at different humidities.

CLAIMS.

1. A polymer suitable for the treatment of human hair, said polymer having the structure I or II below:



and

$$\begin{cases}
\begin{bmatrix}
R \\
CH_2-C \\
C = 0
\end{bmatrix}
\begin{bmatrix}
CH_2-C \\
C = 0
\end{bmatrix}$$
(III)

wherein each G is selected from -OH and  $-OR_3SC_3^-M^+$ ;

each ( is selected from -OR<sub>3</sub>-; -NHR<sub>3</sub>-; -OR<sub>3</sub>NHCONHR<sub>3</sub>=; and -OR<sub>3</sub>NHCOOR<sub>3</sub>-;

each R is H or methyl;

each  $R_1$  is an alkyl of from 1 to 4 carbons;

each  $R_2$  is an alkyl of from 10 to 24 carbons;

each  $R_3$  is an alkylene radical of from 2 to 4 carbons;

J is an anion;

M is a cation:

w, x, y, z, a and b designate the number of moles of the monomeric units in accordance with the mole fraction and mole ratio constraints: w/x and w/y are about 0.4 or greater; w/z is from about 199:1 to about 0.67:1; w/(x + y + z) is from about 199:1 to about 0.25:1, and a/b is from about 199:1 to about 2.3:1, w, z, a and b being positive, and x and y being less than or equal to about 0.5, and

m and n designate the degree of polymerization.

- 2. A polymer as claimed in Claim 1 wherein the mole fractions of W, X, Y, Z, A and B are: W from about 0.2 to about 0.995; z from about 0.005 to about 0.3; a from about 0.7 to about 0.995 and b from about 0.005 to about 0.3.
- 3. A polymer as claimed in Claim 2 wherein the polymer is Polymer (I) and the mole fractions of W, X, Y and Z are: w is from about 0.4 to about 0.95; at least one of x or y is from about 0.1 to about 0.4, and z is from about 0.05 to about 0.2.

- 4. A polymer as claimed in Claim 3 wherein the mole ratio contraints are: w/x from about 9.5:1 to about 1:1, w/y from about 9.5:1 to about 1:1, w/z from about 19:1 to about 2:1, and w/(x + y + z) from about 19:1 to about 0.67:1.
- 5. A polymer as claimed in Claim 4 wherein R is methyl; R

  1 2
  is an alkyl of from 12 to 18 carbons; R is ethyl; J is chloride,

  3
  bromide or iodide, and M is potassium or sodium.
- 6. A polymer as claimed in Claim 2 wherein the polymer is Polymer (II) and the mole fractions of A and B are: a from about 0.8 to about 0.95 and b from about 0.05 to about 0.2.
- 7. A polymer as claimed in Claim 6 wherein the mole ratio of a/b is from about 19:1 to about 4:1.
- 8. A polymer as claimed in Claim 7 wherein R is methyl; R
  1 2
  is an alkyl of from 12 to 18 carbons; R is ethyl; J is chloride,
  3
  bromide or iodide, and M is potassium or sodium.
- 9. An aqueous composition useful as a hair conditioner for human hair and comprising at least one polymer as claimed in any one of Claims 1 to 8 and a cosmetically acceptable aqueous vehicle, said polymer being present in the composition in an amount that is effective when the hair is treated by contact with the composition for from 1 to 30 minutes to improve combability of the hair as compared with hair that has not been so treated.

- 10. A process for conditioning human hair which comprises contacting the hair with an aqueous composition containing at least one polymer as claimed in any one of Claims 1 to 8 and a cosmetically acceptable aqueous vehicle, said polymer being present in the composition in an amount that is effective when the hair is treated by contact with the composition for from 1 to 30 minutes to improve combability of the hair, as compared with hair that has not been so treated.
- 11. A polymer as claimed in Claim 1, substantially as hereinbefore described with particular reference to the Examples.
- 12. A polymer as claimed in Claim 1, substantially as identified as polymer I-1, I-2, I-3, I-4, I-5 or I-6 in the Examples.
- 13. An aqueous composition as claimed in Claim 9, substantially as hereinbefore described with particular reference to the Examples.
- 14. A process as claimed in Claim 10, substantially as hereinbefore described with particular reference to the Examples.
- 15. A process as claimed in Claim 10, substantially as illustrated in any one of the Examples.

## Patents Act 1977 Examiner's report to th Comptroller under Section 17 (The S arch R port)

Application number GB 9222907.9

Relevant Technical fi	ields		Search Examiner
(i, JK Cl (Edition	K )	C3P PDH PDT PDW	
			M J PRICE
(ii) Int CI (Edition	5 )	C08F	
<b>Databases</b> (see over	•)		Date of Search
(i) - i - i - i - i - i - i - i - i - i -			24 DECEMBER 1992
(ii)			

Documents considered relevant following a search in respect of claims 1-15

Category (see over)	Identity of docume	nt and relevant passages	Relevant to claim(s)
Y	GB A 2136689	(L'OREAL) see eg Claim 9 paragraph 11	1 at least
ΑP	EP A2 0464957	(EXXON) the whole document	1 at least
Y	EP A2 0200903	(EASTMAN) see eg Claims 1 and 9	1 at least
Y	US 4818245	(CLAIROL) see eg Claim 9 and the Example	1 at least
		•	
!		·	

<u> </u>	<u> </u>	
Category	Identity of document and r levant passag s	Relevant to claim(s
		,
	•	
:		
	•	

### Cat gories of documents

- X: Document indicating lack of novelty or of inventive step.
- Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.
- A: Document indicating technological back, round and/or state of the art.
- P: Document published on or after the declared priority date but before the filing date of the present application.
- E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.
- &: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).